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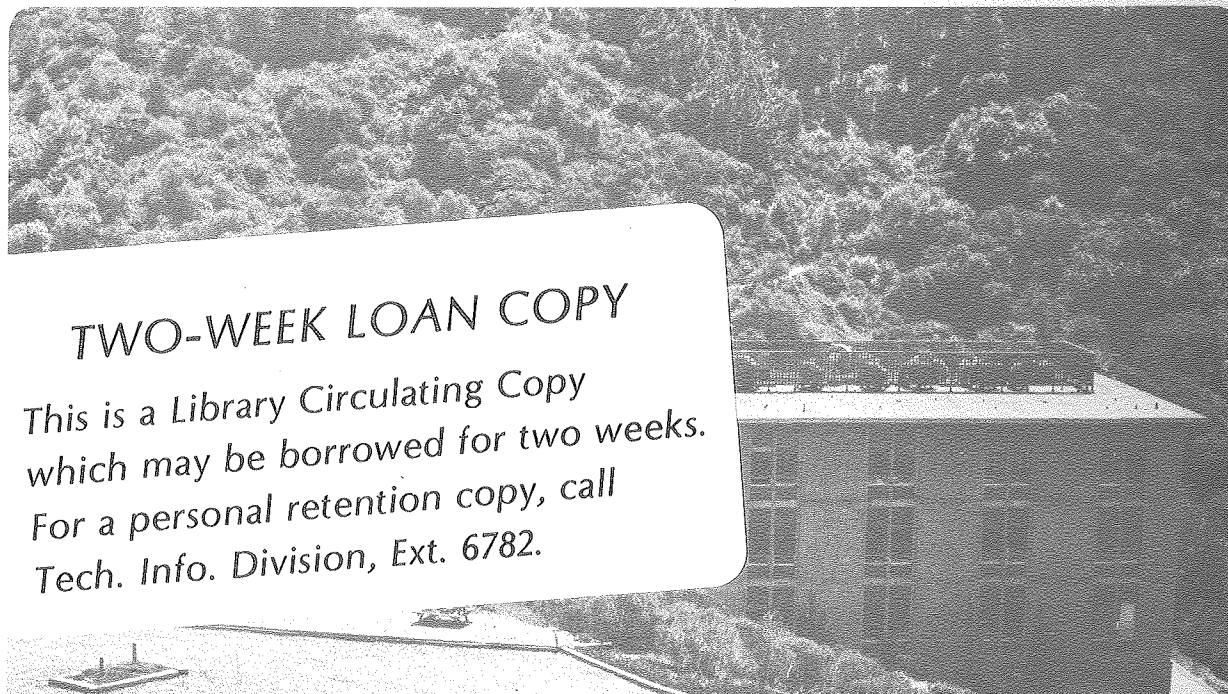
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November 1980



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The Kinetics and Product Yield of the Reaction of HO with HNO_3

by

H. H. Nelson, W. J. Marinelli and H. S. Johnston

Department of Chemistry, University of California,

Materials and Molecular Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

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Abstract

Room temperature rate constants for the reaction $\text{HO} + \text{HNO}_3$ were obtained by laser flash photolysis; HO was observed by resonance fluorescence ($k \pm 2\sigma = 8.2 \pm 1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$); and the product NO_3 was measured by laser absorption ($10.6 \pm 3.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$). The nitrate free radical NO_3 was a major product of the reaction.

1. Introduction

The rate constant for the reaction of hydroxyl radicals with nitric acid



was recently remeasured by Wine et al.¹ and found in their study to be faster than previously accepted at room temperature and to have a negative temperature dependence. The unusually low A factor that was measured has led to speculation about a long-lived intermediate complex which may not decompose to NO_3 and H_2O . Because of the potential importance of these recent results to an understanding of atmospheric chemistry, we have studied this reaction in both the reactant and product channels.

2. Experimental

The techniques of flash photolysis/resonance fluorescence (FP/RF) and flash photolysis/laser absorption (FP/LA) were used to obtain kinetic information by following the time evolution of HO and NO_3 respectively.

The flash photolysis/resonance fluorescence studies were conducted in an apparatus of conventional design.² Hydroxyl radicals were produced by photodissociation of HNO_3 with the output of a Lumonics 860-01 excimer laser operating at 249 nm (KrF). Repetition rates were typically 30 Hz and the output energy was 10-20 mJ. Fluorescence from the 0-0 band of the $\text{HO } A^2\Sigma-X^2\Pi$ system was excited by the output of a microwave driven resonance lamp operating on a 3% $\text{H}_2\text{O}/\text{Ar}$ mixture at a total pressure of 1 torr. A Vycor resonance lamp window was used to block VUV atomic lines and some NO emission which contribute to the background signal. The fluorescence signal was monitored at right angles to the

laser beam and resonance lamp with a detection system that included a CaF_2 window and three baffled, Suprasil-1, f/1 lenses which focus the fluorescence through a 307.2 nm interference filter (20% peak transmission, 10 nm FWHM) onto the cooled cathode of a PMT (RCA C31034) operated in photon counting mode. The time evolution of the fluorescence signal was obtained by recording the photon counting output with an instrument computer operating in the multichannel scaling mode. Typically, the decay following 4096 laser flashes was averaged to obtain a pseudo-first order rate constant.

All experiments were performed in the "slow flow" regime. Nitric acid was entrained in a stream of Ar flowing through a four-pass, non-bubbling, Pyrex saturator. This stream then passed through a 1 m UV absorption cell where the HNO_3 concentration was continuously measured at 200 nm. The output of a deuterium lamp was chopped, focused through the absorption cell, wavelength selected by a McPherson (model 218) 0.3 m monochromator operating with a 0.3 nm bandpass, and detected by a PMT (S-5 response), the output of which was amplified and sent to a lock-in detector. Before and after each decay, pure Ar was flowed through the cell and I_0 measured. The absorption cross section of HNO_3 was measured by titration of the gas stream with NaOH solutions and found to be $6.5 \times 10^{-18} \text{ cm}^2$ under our conditions at 200 nm in agreement with the literature values.^{3,4} The HNO_3 cross sections were also measured in a static, 10 cm cell with a Cary 118 spectrometer in the region 180-210 nm. The result obtained at 185 nm is $1.63 \times 10^{-17} \text{ cm}^2$ which agrees well with the determinations of Wine et al. and Biauume.^{1,5}

After exiting the UV absorption cell, the gas stream entered the 10 cm long photolysis cell equipped with CaF_2 windows. The total pressure in this cell was measured by a MKS Baratron capacitance manometer. Checks were made to insure that the total pressure and HNO_3 concentration were the same in the photolysis cell and the UV absorption cell under the flow conditions used.

The flash photolysis/laser absorption experiments were conducted in a single-pass, jacketed, 1.9 m absorption cell. Nitric acid, entrained in a slow flow (~ 280 standard $\text{cm}^3 \text{min}^{-1}$) of N_2 passed through a saturator at 250 K, flowed through the cell at 10 torr total pressure, and was photolyzed by output of the excimer laser operating at 249 nm. Approximately 0.04% of the HNO_3 in the beam was photolyzed per 10–20 mJ shot at repetition rates of 1–2 Hz. The energy of each photolysis pulse was measured using an energy meter located at the cell exit, and a suitable model of photolysis–laser–beam divergence was used to calculate an averaged fluence. Typical HNO_3 concentrations ranged from about 8×10^{15} to 4×10^{16} molecules cm^{-3} and were determined by continuously monitoring the exhaust from the photolysis cell at 215 nm in a 1 m UV absorption cell similar to the one previously described. The absorption cross section used at 215 nm was that of Molina and Molina³ ($3.56 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$) which is in good agreement with Johnston and Graham.⁴ A pressure drop was found to exist between the photolysis and monitoring cells; its magnitude was determined by flowing a standard mixture of NO_2 in N_2 through both cells under experimental conditions and obtaining the relative NO_2 concentrations via absorption of the 488 nm output of an Ar ion laser. The results are adjusted to reflect this factor.

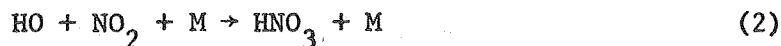
The NO_3 produced from the reaction of HO with HNO_3 was monitored by observing the absorption of the CW output from a Spectra-Physics Model 375 dye laser propagated coaxially to the photolysis beam and operating on R6G dye at 623.5 nm, the NO_3 A-X v_1 (1-0) transition. The bandwidth of the laser was approximately 0.29 nm. The dye laser output was monitored by an EG&G SGD-100A silicon photodiode coupled to a pre-amplifier of in-house design having a total system bandwidth of 1 MHz. The output from the preamplifier was recorded by a 9 bit A-D converter interfaced to a multichannel scaler. A typical experiment was the sum of 256 shots.

The Ar used in this study had a stated purity of > 99.999% and the N_2 99.998%; both were used without further purification. The HNO_3 was distilled from mixtures of NaNO_3 or KNO_3 in 96% H_2SO_4 under vacuum. The product was collected at 250 K with only the middle portion saved. The nitric acid invariably contained 0.1-0.2% NO_2 impurity as measured by its 350 nm absorption; storage at 196 K had no effect on the purity.

3. Results and Discussion

All experiments in the flash photolysis/resonance fluorescence study were performed under pseudo-first order conditions with $[\text{HNO}_3] > 1000 [\text{HO}]$. A typical semilogarithmic HO decay plot is shown in Fig. 1. The decay is linear over 2 to 3 $1/e$ times.

The bimolecular rate constant was determined at 3 total pressures and for a 21 fold range of HNO_3 concentration. The observed HO decay times were corrected for the contribution of the $\text{HO} + \text{NO}_2$ recombination reaction



using recommended values of the reaction rate constant as a function of pressure.⁶ These data are shown plotted vs HNO_3 concentration in Fig. 2. The rate constants calculated are $8.0 \pm 0.3 \times 10^{-14}$, $9.2 \pm 0.56 \times 10^{-14}$, and $7.5 \pm 0.89 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 10, 25, and 50 torr total pressure respectively. The uncertainties are twice the standard deviation and do not include systematic errors. The non-zero intercepts are a result of HO diffusion from the product viewing zone and reaction with impurities in the Ar carrier gas.

To calibrate this experimental system of resonance fluorescence, it was used to study the reaction of hydroxyl radicals with hydrogen peroxide ($\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HOO}$), where H_2O_2 was monitored by absorption at 200 nm ($4.67 \times 10^{-19} \text{ cm}^2$), at concentrations between 3.1×10^{14} and $2.1 \times 10^{15} \text{ cm}^{-3}$, with 10 torr Ar total pressure, and at 295 K. The second order rate constant ($\pm 2\sigma$) was found to be $1.57 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, in agreement with recent literature values.^{7,8}

The data in the NO_3 absorption experiments were recorded in transmission mode (Fig. 3a) and converted to optical density [$D = \ln(I_0/I)$] by using the transmission during the pretrigger period as I_0 (Fig. 3b). Experimental runs were performed with 20 ms sweep times; however longer sweep times were explored to insure that the signal returned to baseline between flashes. The time evolution of the NO_3 optical density was analyzed by fitting it to the expression

$$D(t) = D_A \left(e^{-k_r t} - e^{-k' t} \right) \quad (3)$$

where k' is the pseudo-first-order rate constant for reaction (1), k_r is the first-order rate constant for removal of NO_3 (diffusion from the viewing area, reaction with trace amounts of NO_2 , NO , or other species) and D_A would be the asymptotic optical density of NO_3 if the removal processes k_r had negligible rates. A non-linear, least square, iteration method was used to fit D_A , k_r , and k' to the experimental data and that fit is included in Fig. 3b. These fits converged to a unique solution for a wide range (10x) of initial inputs for the fitting parameters. For each experiment i the second-order rate constant k_1 for reaction (1) is related to the pseudo-first-order rate constant by

$$k_{1i} = k_i' / [\text{HNO}_3]_i \quad (4)$$

The values of k_1 are plotted against nitric acid to show the lack of trend with nitric acid concentration, Fig. 4. The average of these results ($\pm 2\sigma$) is $10.6 \pm 3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The NO_3 product yield (ϕ) from reaction (1) relative to the number of photons absorbed by nitric acid is given by

$$\phi = \left(\frac{D_A}{\sigma_{\text{NO}_3} L} \right) \cdot \frac{1}{E [\text{HNO}_3] \sigma_{\text{HNO}_3}} \quad (5)$$

where L is the optical pathlength (193 cm), σ_{HNO_3} is the absorption cross section of Molina and Molina³ at 250 nm ($2.0 \times 10^{-20} \text{ cm}^2$), E is the laser fluence in photons/ cm^2 , and σ_{NO_3} is the NO_3 cross section at 623.5 nm, the probe wavelength used in these experiments. For 15 determinations the average NO_3 quantum yield ($\pm 2\sigma$) is 1.34 ± 0.18 using σ_{NO_3} from Graham and Johnston⁹ ($1.2 \times 10^{-17} \text{ cm}^2$), 1.53 ± 0.21 using σ_{NO_3} from

Mitchell et al.¹⁰ ($1.05 \times 10^{-17} \text{ cm}^2$), or 0.92 ± 0.12 using the change proposed by Magnotta¹¹ for the results of Graham and Johnston.⁹ Since there are no known chain mechanism that would result in a quantum yield greater than one; it must be assumed that there is some systematic error. The two most likely quantities to be questioned here are the intensity of the laser pulse and the value of σ_{NO_3} under our experimental conditions. The divergence of the excimer laser in the 193 cm absorption cell is difficult to model and some additional HNO_3 photolysis due to window or other internal reflections cannot be entirely discounted. The range of values reported for σ_{NO_3} under varying experimental conditions of bandwidth, pressure, and optical density also contribute to the uncertainty of this result. While the NO_3 quantum yield cannot be precisely determined from these results, it is clear that NO_3 was produced at a rate comparable to that of HO loss ($10.6 \pm 3.4 \times 10^{-14}$ relative to $8.2 \pm 1.8 \times 10^{-14}$) and with a product quantum yield comparable to one. Thus the major product channel of reaction (1) is confirmed to be formation of H_2O and NO_3 .

The room temperature rate constants for the reaction of HO with HNO_3 determined in this work are $8.2 \pm 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (FP/RF) and $10.6 \pm 3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (FP/LA). Given some of the experimental difficulties encountered in the FP/LA experiments, we feel that the FP/RF experiments are more accurate as well as more precise. The rate constant measured in the FP/RF experiment is in agreement with Smith and Zellner¹² (8.0×10^{-14}) and Margitan, Kaufman and Anderson¹³ (8.9×10^{-14}), but it disagrees with the results of Wine

et al.¹ (12.5×10^{-14}). However the value of k_1 determined by Wine et al. does fall within the upper error limit of the FP/LA result. Measurement of the temperature dependence of this reaction is currently being carried out in this laboratory.

4. Acknowledgments

This material is based upon work supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48. The excimer laser was obtained for one month as a loan from the San Francisco Laser Center, which is supported by the National Science Foundation under Grant No. CHE 79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

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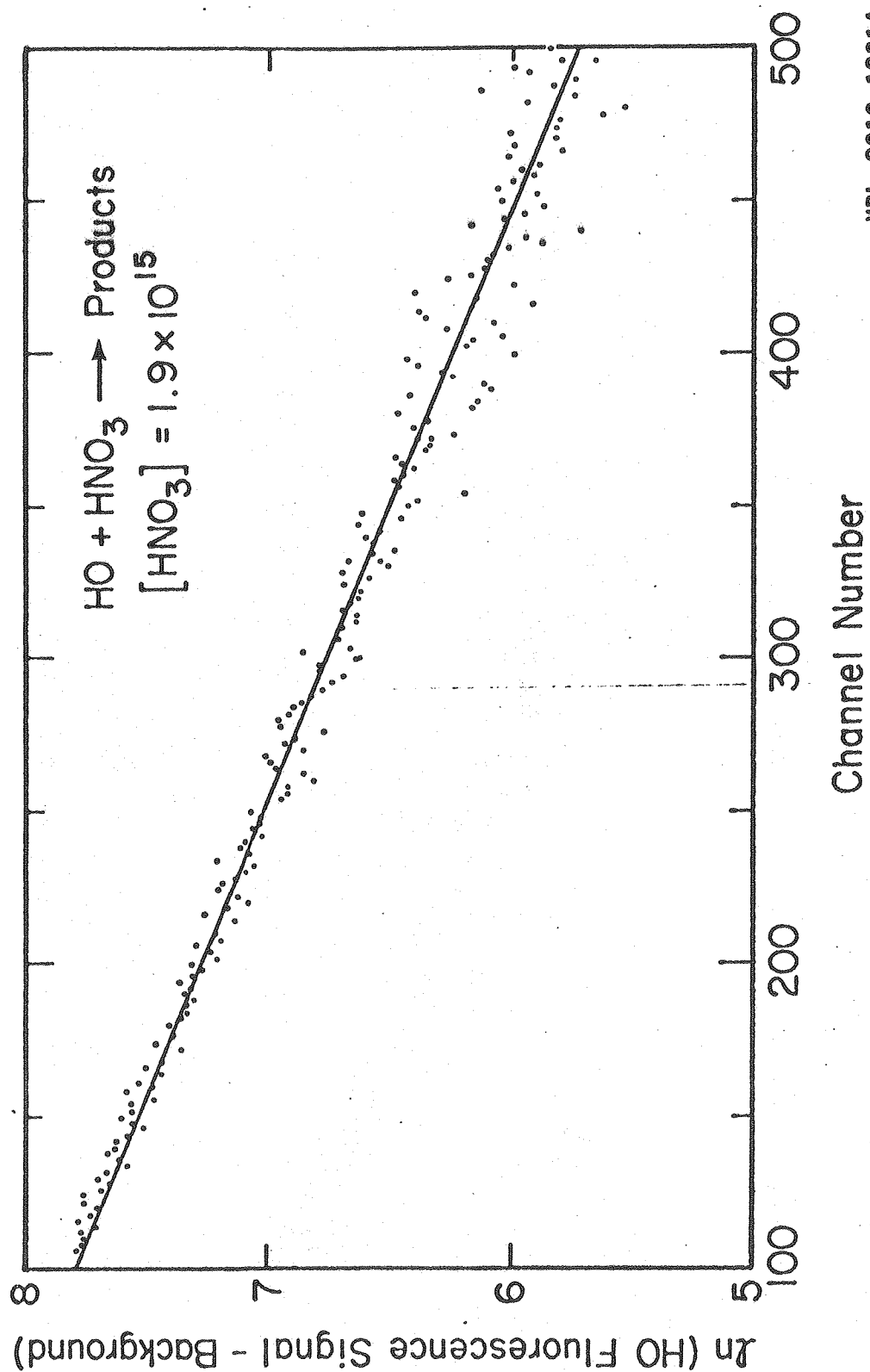
Figure Captions

Figure 1. A typical semilogarithmic HO decay plot from the flash photolysis/resonance fluorescence experiments with the line fit to the data by linear least squares methods.

Figure 2. Pseudo first-order rate constant k' plotted against the concentration of nitric acid obtained in the flash photolysis/resonance fluorescence experiments at 10, 25, and 50 Torr total pressure. A linear least-squares fit to each data set results in the lines shown.

Figure 3. (a) Data as recorded in transmission mode for NO_3 laser absorption. (b) Data converted to optical density ($\ln I_0/I$) and computer fit to expression (3).

Figure 4. Second order rate constants for $\text{HO} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$ as determined in flash-photolysis/laser-absorption experiments.



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Figure 1

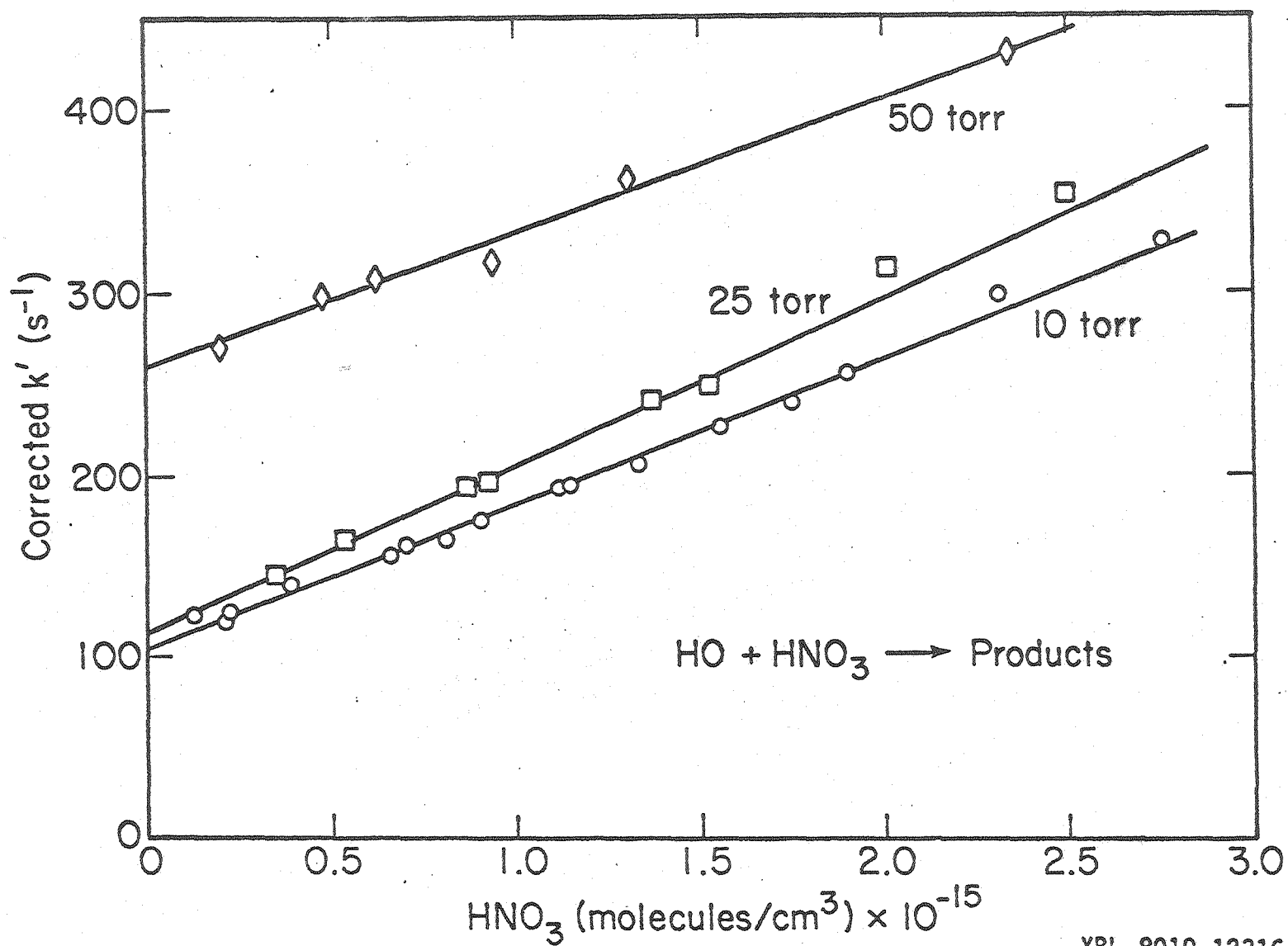


Figure 2

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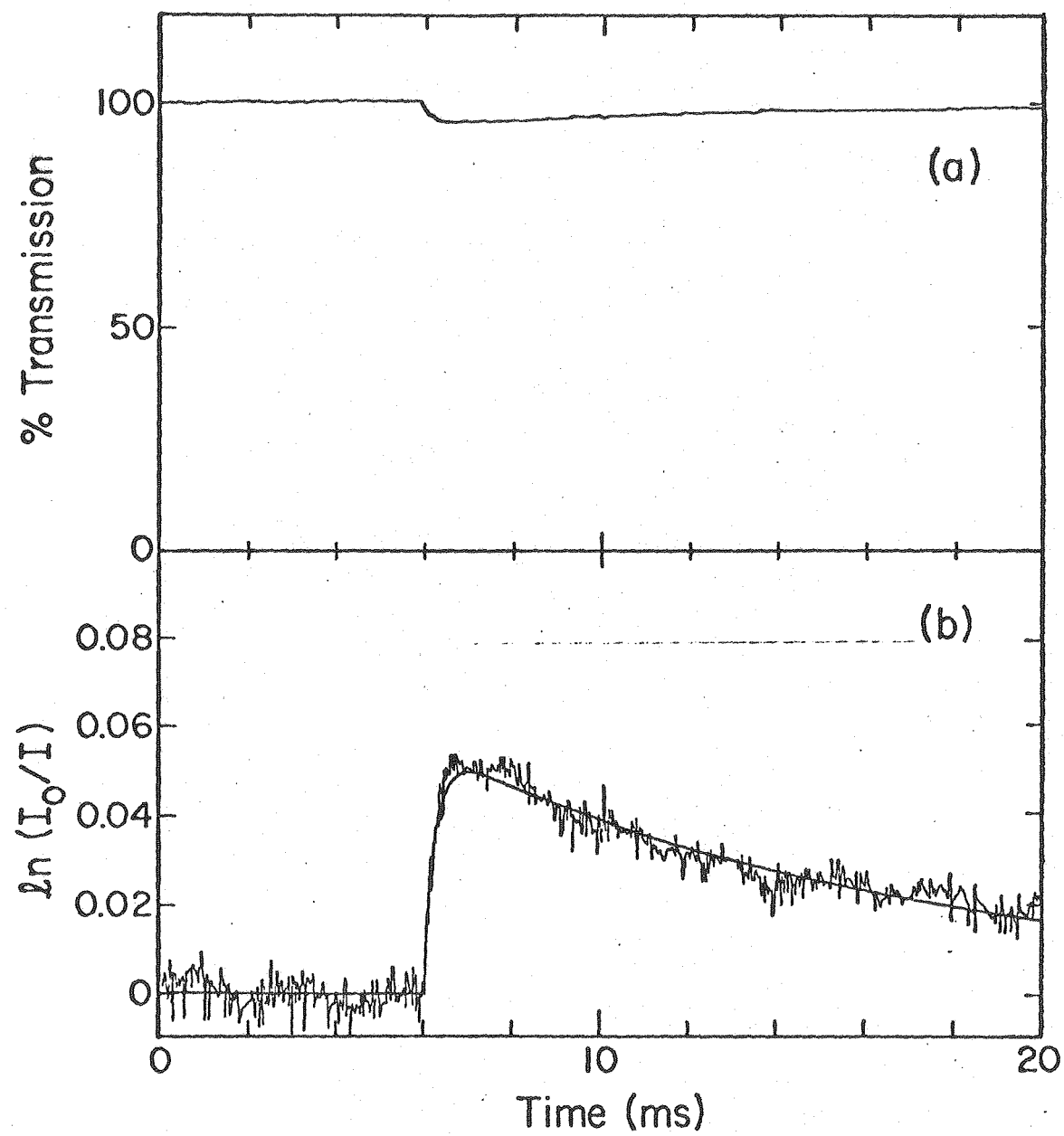
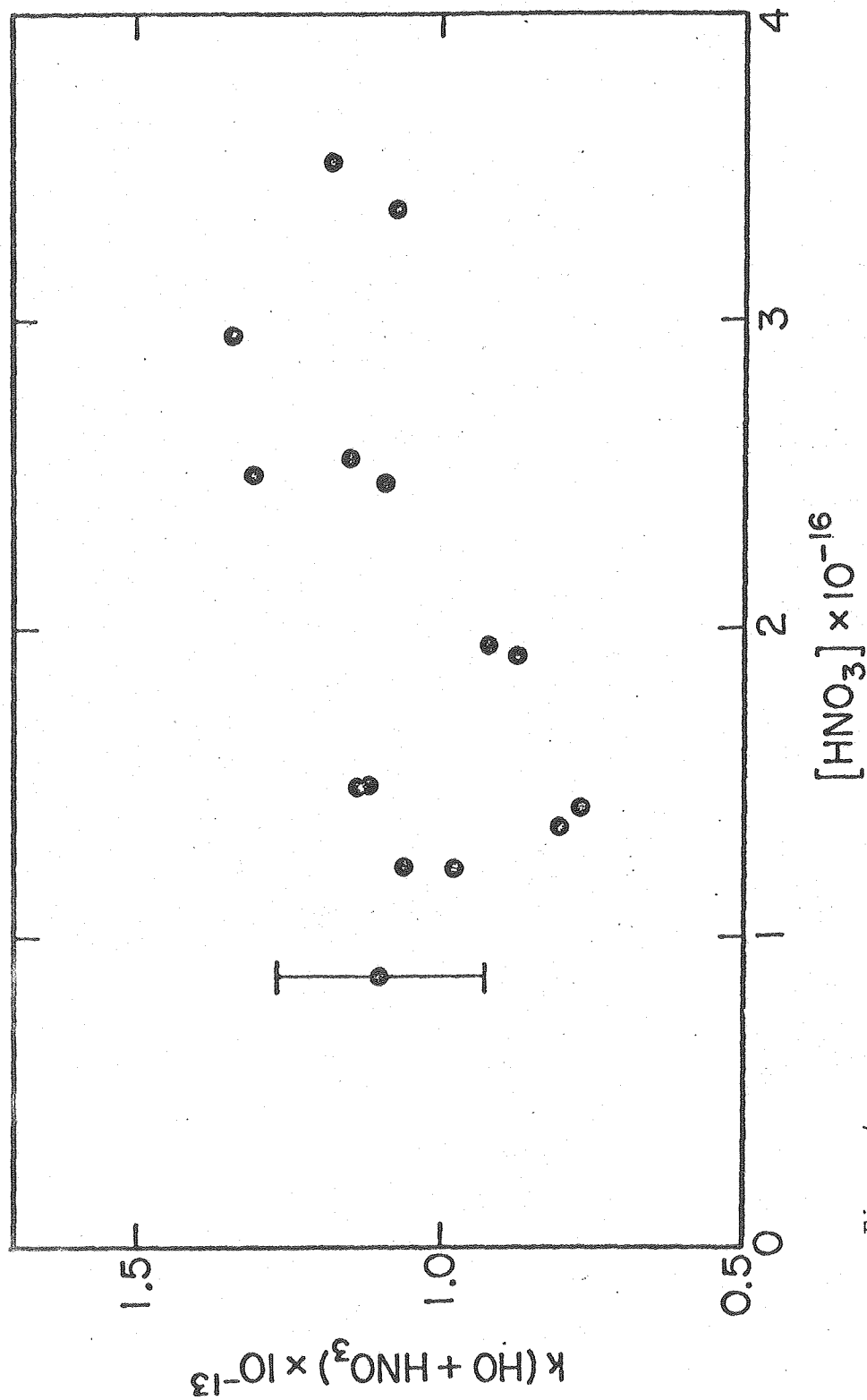


Figure 3

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Figure 4